Far Infrared Spectroelectrochemistry of Nitrogenase Model Complexes

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Nitrogenase is an enzyme that is able to catalyze the efficient reduction of dinitrogen to ammonia. It is also able to reduce a number of other substrates (pseudo-substrates) such as hydrogen ion and acetylene. The active site of nitrogenase contains a Mo/Fe/S cluster. This cluster can be extruded from the protein (FeMoco) and isolated. Inorganic chemists have been unsuccessful in synthesizing the cofactor (FeMoco), but have been able to characterize other Mo/Fe/S clusters which are able to reduce nitrogenase pseudo-substrates. Very little mechanistic detail is known about the reduction of substrates or pseudo-substrates by the enzyme, cofactor or models.

Infrared spectroelectrochemistry is ideally suited for the investigation of this problem. The reduction of the complex should lead to characteristic changes in the core vibrations of the cluster which can be used to characterize the overall oxidation states of the complex. When these experiments are repeated in the presence of pseudo-substrates, it should be possible to determine the oxidation state of intermediates in the catalysis. The first step in this process, though, is the characterization of the reduced cluster species. The vibrations for the Mo/Fe/S cluster are all in the far infrared (100-600 cm^{-1}), a region that has been rarely exploited by spectroelechemistry. More polar solvents such as DMF and acetonitrile are not transparent in this region. Other common electrochemical solvents such are methylene chloride and THF have few bands in this region.

The initial studies were carried out using linear metal clusters such as $[Cl_2FeS_2MoS_2Cl_2]^{2-}$ (*1*). This complex was chosen as the initial species in that it was synthetically easy and its vibrations were of high enough energy to be observed using a conventional instrument and cell. The difference spectra during the thin layer spectroelectrochemical reduction at the first wave of the complex are shown in Figure 2. Negative bands are due to the disappearance of vibrational bands, while positive bands are due to the new species. The band at 514 cm^{-1} is not due to the complex, but changes in the electrolyte concentration. The band at 474 cm^{-1} is due to the bridging sulfur vibrations. This band decreases upon reduction, and a new broad band at 449 cm^{-1} appears. The thin layer spectroelectrochemical experiment was repeated using the ^{34}S isotope, and the expected shifts in the sulfur vibrations was observed. The results are summarized in Table 1.

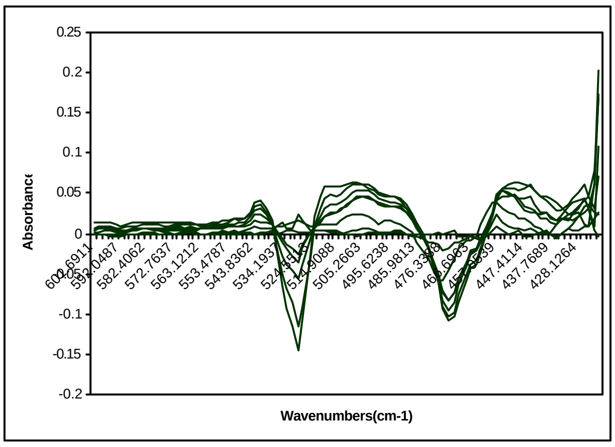

Figure 1

Compound	Infrared Bands (cm^{-1})
complex *1* (^{32}S)	474
reduced complex *1* (^{32}S)	457
complex *1* (^{34}S)	464
reduced complex *1* (^{34}S)	449

The exact structure of the reduced complex has not yet been completely elucidated, but the most likely structure is probably a cubane complex.

Additional work will be reported on the thin-layer far infrared spectroelectrochemistry of 4Fe-4S and Mo-3Fe-4S clusters. These complexes are all reversible on the spectroelectrochemical time scale and their vibrations are predominantly between 200-400 cm^{-1}. Analysis of the vibrations based on isotopic substitution will be presented.